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ORIGINAL PAPER

Process Development Unit (PDU) for Hydrothermal Carbonization (HTC) of Lignocellulosic Biomass

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Abstract Hydrothermal carbonization (HTC) is an effective means of upgrading raw lignocellulosic biomass to a more uniform solid hydrochar, having increased energy density. The HTC process is conducted in hot (200–300 °C) pressurized liquid water. Most experimental investigations of HTC have been conducted at small scale, using bench-top batch reactor vessels. In this work, we report the design, fabrication, and demonstration of a larger-scale process development unit (PDU) that enables semi-continuous HTC treatment of approximately 3 kg of biomass. This auger-equipped tubular reactor system conveys raw biomass through a zone of hot pressurized water, and deposits the solid hydrochar product in an accumulator vessel that is maintained at a lower temperature. Gaseous and liquid samples can be collected both while the PDU is at operating temperature, and after it has cooled. Characterization of gaseous, aqueous, and solid samples from a set of PDU experiments indicated good agreement with results from previous HTC experiments conducted in a much smaller (2-L) batch reactor. This suggests that the PDU provides a reliable scale-up of the HTC process.

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Introduction

Various methods have been developed to thermally pretreat lignocellulosic biomass, converting it to a solid material having higher energy density and improved handling properties compared to raw feedstock. One such method that has recently gained considerable attention is hydrothermal carbonization (HTC), which is also known as wet torrefaction, coalification, hot compressed water (HCW) treatment, and other names. HTC involves treatment of raw biomass feedstock in hot, pressurized liquid water. Typical process temperatures are 200–300 °C, with reaction times from a few minutes to several hours [1, 2]. In addition to the solid hydrochar product (also known as bio-char, bio-coal, HTC-char, and other names), the HTC process produces gases (mainly CO_2) and a wide variety of water soluble organic products, including sugars, acids, furans, furfurals, etc. An advantage of HTC over other biomass treatment methods is its accommodation of wet feedstocks, thus avoiding the complexity and costs of predrying the raw lignocellulosic biomass. Several excellent reviews of the HTC process are available in the literature [1–5].

To our knowledge, there are no full-scale, commercial operations of HTC in existence today, although numerous modeling studies have been conducted to investigate hypothetical HTC plants [6–9]. Most experimental investigations of the HTC process and products have been conducted in a batch mode, using laboratory-scale autoclave reactors—generally with capacities of 2-L or less. We also have conducted previous HTC research using 2-L

Parr pressure vessels [10, 11]. However, to advance knowledge of the HTC process under more commercially-relevant conditions, it is necessary to explore larger-scale operations. Thus, we have undertaken an effort to scale-up the HTC process by a factor of 20 compared to our earlier 2-L Parr process, and to develop a semi-continuous method of treating raw feedstock, as opposed to earlier batch methods. The specific objectives of this work were to: (1) design and build a small, semi-continuous HTC PDU, (2) demonstrate satisfactory operation of the PDU, and (3) compare the PDU performance and products with those typically observed from use of laboratory-scale, stirred pressure vessels (Parr reactors).

Design and Fabrication of PDU

A major challenge for a small-scale, continuous PDU is effectively conveying solid materials across pressure boundaries. When operating at 300 °C, the pressure inside an HTC process unit is approximately 1,300 psi (9.0 MPa). In a recent report describing HTC of woody biomass and coal, this was addressed by producing aqueous slurries of finely milled feedstocks, and using a slurry pump to feed into the reactor [12]. However, for larger-sized wood chips, this method is not feasible. In full, commercial-scale HTC treatment of wood chips, some type of lock-hopper arrangement would likely be employed to continuously move feedstock into the hot, pressurized reactor zone, and move hydrochar product out of the reactor. Thomsen et al. [13, 14] have described such a method involving screw conveyers to move straw into and out of hydrothermal zones in a pilot plant operation.

Because of technical difficulties (and high expense) that pressure feeding entails in a small-scale reactor system, we avoided the complication of maintaining different pressure zones within the PDU. Instead, the PDU consisted of a single pressure regime, but with the ability to move solid feedstocks and products into and out of the reaction zone that contained hot, pressurized liquid water. This was achieved using a "V" shaped tubular reactor system in which liquid water was confined to the bottom of the "V". An inclined auger was used to feed raw biomass into the hot reaction zone, with a second inclined auger used to convey treated biomass out of the reaction zone and deposit the wet hydrochar product into a collection vessel (accumulator).

A schematic of the PDU is provided in Fig. 1. Fabrication of the main pressure vessel comprising the PDU was outsourced to Custom Metalcraft (Springfield, MO, USA). The main body of the reactor consists of Schedule 80, 316 stainless steel pipe; the auger sections being 4-in IPS diameter and the accumulator being 6-in IPS diameter. Pipe connectors from Grayloc Products (Houston, TX) were used to connect the different segments of the PDU. These fittings can be connected and disconnected quite easily, which is convenient because three of them must be manipulated during each run of the PDU—for feedstock addition and product removal.

To accommodate the desired 2–3 kg of feedstock, the feed side of the PDU (Zones 1 and 2 in Fig. 1) is approximately 2.4 m (8 ft.) in length, and contains an auger with 1.8 m (6 ft.) of flights. The reactor side of the PDU (Zones 3 and 4 in Fig. 1) is approximately 1.5 m (5 ft.) in length, with 1.1 m (3.5 ft.) of flights. The augers are operated with Dayton ½ HP, 90 V permanent magnet DC motors and variable speed DC controls (Dart Controls), both purchased from Grainger (Lake Forest, IL, USA). To control the PDU reaction temperature, a series of electric band heaters were installed (Tempco Electric Heater Corp., Wood Dale, IL, USA). These heaters are arranged to independently heat five zones throughout the reactor unit.

In addition to the band thermocouples, thermocouples are inserted through ports in the PDU to measure internal temperatures at five separate locations. Figure 1 shows the locations of these heating bands in each of the five heating zones, as well as the five thermocouples. Through experimentation, optimum locations of these heating bands were determined to achieve rapid heat-up times and consistent temperature profiles throughout the reactor system. Minimal heating was required at the top of the feed auger and in the accumulator vessel (Zone 5 in Fig. 1), with maximum heating required near the bottom of the reactor, where the liquid water was contained. As shown in Fig. 1, most of the fourteen heating bands were located in Zones 2, 3, and 4. More details about the design and operation of the PDU are provided in the Supplementary Material, which also includes a number of CAD drawings of various components.

Due to the non-uniformity of temperatures measured by different thermocouples throughout the PDU, it is necessary to define a specific "reaction temperature." For this purpose, we calculated temperature, based upon measured pressure levels, as pressure is consistent throughout the PDU under these equilibrium saturation pressure conditions. The pressure transducer located at the top of Zone 5 (at Port P-5A) was used as the basis for this calculation, which utilized the Antoine equation:

$$\log_{10} P = A - \frac{B}{C + T}, \text{ which solving for temperature gives:}$$

$$T = \frac{B}{A - \log_{10} P} - C$$

In these equations, P = pressure (mm Hg); T = temperature (°C); A, B, and C are component-specific constants. (Further details of this calculation are provided in the Supplementary

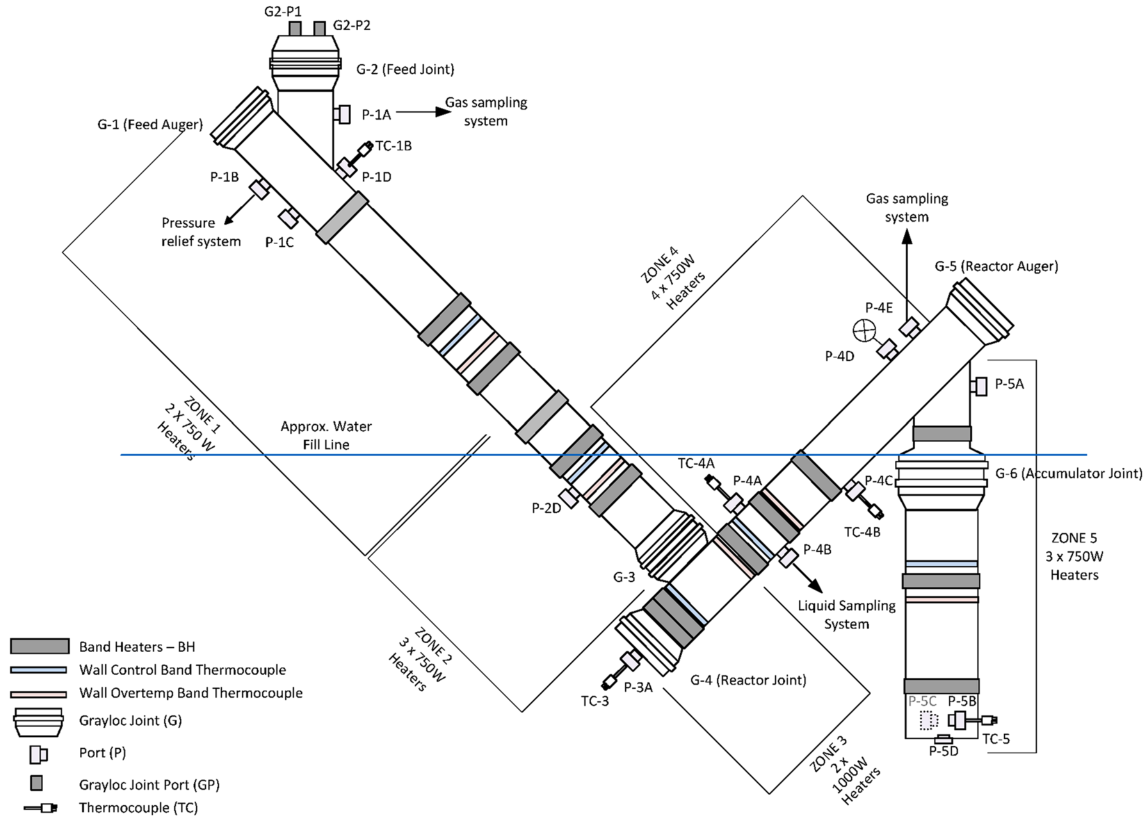


Fig. 1 Schematic of PDU showing heating zones, ports, fittings, and sampling locations. Drawing not to scale

Material.) In calculating the PDU reaction temperature, specific constants for water are used for A, B, and C. However, in the HTC process, other gases (primarily CO_2) are produced. Consequently, the pressure at a given temperature is slightly higher than it would be without these gaseous products, and the calculated temperature is thus overestimated to a small extent. With earlier HTC experiments using a 2-L Parr pressure reactor (where temperatures were more uniform), we typically measured pressures that exceeded the calculated saturated steam pressure by 25–50 psi (0.17–0.34 MPa) at reaction temperatures of 255–275 °C.) However, given the non-homogeneity of temperature within the PDU, we believe this method of calculating a reaction temperature is the most practical and repeatable approach.

Not shown in Fig. 1 is the complex electrical system used to control and monitor operation of the PDU. Heating of the PDU is done with electrical heating bands placed around the outside of the pressure vessel. Both 750-W and 1,000-W band heaters are used. Five different heating zones are identified, with each zone having several heating bands powered by a single control module. Each of the five zones also has a band thermocouple to measure the surface temperature of the reactor, and prevent overheating of the steel pipe. Electrical wiring diagrams for the heater system are provided in the Supplementary Material. Photos of the PDU are provided in Fig. 2.

Gas and Liquid Sampling Systems

The PDU was designed to allow for sampling of gaseous and liquid products while operating in a hot, pressurized mode. The gas sampling system consists of a 1-L Parr pressure vessel that is connected, through a high pressure valve and ¼ in. stainless steel tubing, to a port near the top of the feed assembly (Port P-1A in Fig. 1). The head of the Parr vessel was also connected, through a high pressure valve, to a vent line that could be sampled into a Tedlar bag. To collect a sample of hot process gas (typically at the end of the run, when the heaters and augers are turned off), the upstream valve between the PDU and the Parr vessel is briefly opened to pressurize the 1-L gas sampling vessel. After the PDU has cooled (typically the following day), the downstream valve is opened to release the pressurized gas into the Tedlar bag, while condensed water remains behind in the Parr vessel. Cooled headspace gas remaining in the PDU is collected by venting the PDU through the same 1-L Parr vessel. More details and photos of this gas sampling system are provided in the Supplementary Material.

The liquid sampling vessel consists of a cylindrical pressure vessel, with high pressure valves on both ends. This vessel was connected to the PDU, with stainless steel tubing, at a port located in Zone 4, partway up the reactor auger, at a point that was expected to always be beneath the

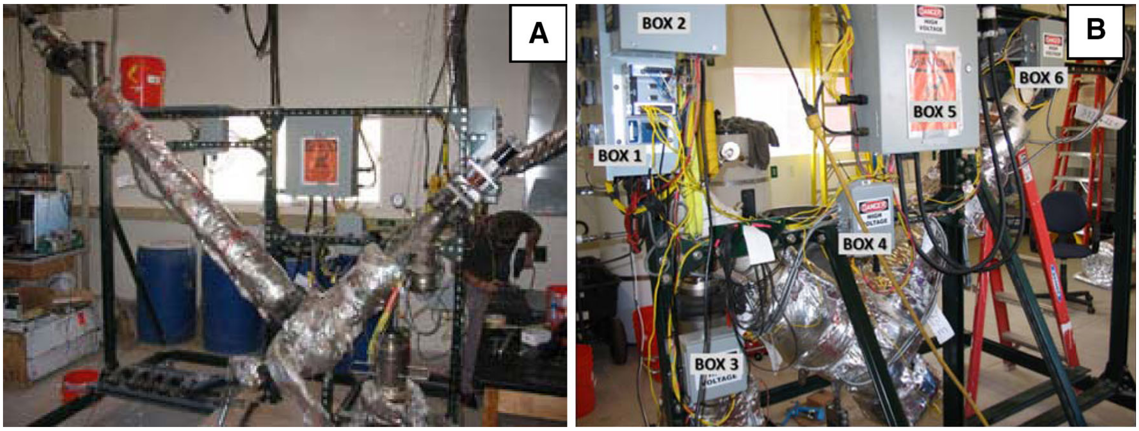


Fig. 2 Photos of completed PDU: **a** Front view. **b** Back view, showing control boxes for heaters and other system components

water level (Port P-4B in Fig. 1). At the end of an HTC experiment (at the same time the pressurized gas sample is collected) the upstream valve is briefly opened to allow hot, pressurized liquid to enter the liquid collection vessel. After cooling the PDU (typically the following day), the sampling vessel is removed and the collected liquid is drained into a beaker for subsequent analysis. The PDU is then opened to collect additional liquid samples from the bottom of the PDU reactor (Port P-3A) and from the accumulator vessel. More details and photos of this liquid sampling system are provided in the Supplementary Material.

Optimization of PDU Operation

Once the PDU pressure vessel was received from Custom Metalcraft, it was mounted on a steel frame that had been prepared for it, and various additional components were attached—including heating bands, thermocouples, auger motors, insulation, gas sampling system, and hot liquid sampling system. Following this, several experiments were conducted to define and optimize operating procedures.

Before operating the PDU in a fully hot, pressurized mode, numerous check-out tests were performed to ensure satisfactory operation of individual components, such as the auger motors, heaters, electronic control system, data acquisition system, and other mechanical and electrical components; and to become familiar with loading and unloading the unit. This troubleshooting activity uncovered numerous problems, all of which were eventually solved.

Not unexpectedly, biomass feeding and conveyance problems were encountered, and several approaches were used to overcome them. Feeding of the PDU requires an operator (standing on a ladder) to drop handfuls of wood chips into the feeding port, while activating the feed auger between increments of feedstock. Several feedstock loading methods were tried—including wet loading, dry loading, use of different wood chip sizes, and various manipulations of the auger while loading. From these experiments it was determined that small chips ("micro-chips" of about 1/4–3/8 in. size) load much better than larger ones (conventional chips of 1/2–3/4 in. size). Also, feeding of dry chips is more convenient than feeding of wet chips. Once the feedstock has been loaded (typically about 3 kg), the desired amount of hot water is added through the same feed port. This port is then sealed with a Grayloc fitting cap (feed joint G2 in Fig. 1) and the heating system is activated.

During operation of the PDU, some wood chips adhere quite strongly to surfaces of the feed auger, making it difficult to completely transfer all biomass from the feed side to the reactor side of the PDU. To address this problem, a layer of 1-in. glass balls was added on top of the woodchips after they had been loaded into the auger. At the end of a PDU run, these balls are recovered in the accumulator vessel, along with the produced hydrochar. This method is helpful in pushing the biomass feed into the reactor, and minimizing the amount of feedstock and hydrochar that is retained on the auger surfaces and reactor walls.

High quality, effective insulation is necessary to maintain temperature control and achieve rapid heat-up of the PDU. For this purpose, Thermal Ceramics FireMaster FastWrap XL was used. This material contains fiberglass enclosed in foil, and is easy to handle and cut into various shapes to better fit the geometry of the PDU. Although the insulation itself is rated to 1,200 °C, the foil wrapping (which is used to aid in safe handling of the insulation) degrades above 250 °C. Therefore, the PDU was first covered with header wrap (a woven, composite fibrous glass that can tolerate temperatures up to 1,100 °C), so that the foil does not directly contact the band heaters.

Removing wet hydrochar from the PDU accumulator is challenging. Even when empty, this vessel weighs almost 50 kg, making it difficult to tip upside down and scoop out (or wash out) the product. The most effective solution involves a combination of a hoist, a saw horse, and a custom made scoop. Some hydrochar product also remains within the reactor auger, where it strongly adheres to the auger surfaces. Initial attempts to collect this hydrochar (without needing to completely remove the auger) involved spraying with pressurized water. However, this was not very effective, as the pressurized water cannot penetrate through the entire auger. A more successful method is to dry the auger with hot air, then run the auger in reverse and collect the dry solid as it falls out the bottom of the PDU.

Results and Discussion of PDU Operation

To demonstrate satisfactory operation of the PDU, a matrix of 4 HTC experiments was conducted using Slash Pine micro-chips as feedstock. In these experiments, the reactor temperature and auger speed were varied as shown in Table 1. Based upon experiments in which glass marbles were placed at the top of the biomass feed, it was determined that the fast auger speed corresponds to a residence time of approximately 6 min, while the slow speed corresponds to a residence time of approximately 12 min (measured as elapsed time between starting the augers and the first marbles dropping into the accumulator).

Following each experiment, the PDU was allowed to cool overnight and was then vented to release gaseous products. (No efforts were made to collect the gaseous products from this set of experiments.) A port at the bottom of the PDU was opened to drain most of the water (Port P-3A in Fig. 1). The accumulator was then removed, and its contents were filtered to recover the hydrochar product. Additional hydrochar was recovered by running the reactor auger in reverse, and collecting the solid material that fell out the bottom of the reactor. Following this, the feed auger was activated, and additional solids that fell out the bottom of the reactor were collected. The PDU was left in an open configuration for at least 24-h, allowing the inside to completely dry out. This drying released a small amount of additional hydrochar that had adhered to the auger and reactor walls. Compressed air was used to blow this material out the bottom of the reactor. Thus, at the end of each experiment, the total hydrochar was collected in four fractions: accumulator, reactor auger, feed auger, and wall residues.

Table 1 Matrix of PDU experiments with Slash Pine

Run no.	Feedstock mass, kg	Reactor temp., °C	Auger speed
1512	2.615	235	Slow
1513	1.787	235	Fast
1514	2.112	275	Slow
1515	1.371	275	Fast

Hydrochar Results

The mass recovery and energy content of the hydrochar collected in each of the four fractions described above are shown in Table 2. These results demonstrate that most of the recovered hydrochar was obtained from the accumulator, as desired, although a significant amount was also obtained from the reactor auger. Relatively little char was obtained from either the feed auger or the wall residues. Expected differences are seen between chars produced at low and high temperatures. At higher temperatures, total recovery of hydrochar is reduced, but the energy content of the hydrochar is increased. The energy contents of about 22–24 MJ/kg (HHV) at 235 °C and 28–29 MJ/kg at 275 °C are in good agreement with values obtained previously from treatment of woody biomass in a 2-L stirred Parr reactor [10, 11]. The ease of pelletization, and the robust nature of pellets produced from the PDU hydrochar are also similar to what was observed with hydrochar produced in the Parr reactor. (Pelletization results will be reported separately.) This gives us confidence that HTC results obtained using other feedstocks in the Parr reactor are also transferrable to the PDU.

No consistent effects of auger speed were observed in these reactions. Total hydrochar recovery was somewhat higher using the slow auger speed at 235 °C, but not at 275 °C. Also, the energy contents of all char fractions were very similar between the two speed conditions. Thus, it appears that the effects of auger speed (or residence time) are small in comparison to the effects of reaction temperature. Based upon these results, it was decided that all four hydrochar fractions from a single HTC experiment within the PDU could simply be combined and characterized together, thereby simplifying sample handling logistics and minimizing laboratory expenses.

The effects of PDU reaction temperature upon energy densification of the hydrochar products are illustrated in Fig. 3, where comparisons are shown with results obtained in previous HTC experiments using a 2-L stirred Parr reactor [11]. In these earlier experiments, the three woody feedstocks (Tahoe Mix, Loblolly Pine, and Pinyon-Juniper) gave relatively consistent increases in energy density with increasing process temperature. The energy density results from these PDU experiments fall within the same range as observed earlier.

Additional laboratory analyses were conducted to characterize the solid and aqueous products from these four

Table 2 Hydrochar recovery from PDU experiments with Slash Pine micro-chips

Hydrochar fractions	235 °C reactor temperature				275 °C reactor temperature			
	Slow augers		Fast augers		Slow augers		Fast augers	
	Mass, %	HHV, MJ/kg	Mass, %	HHV, MJ/kg	Mass, %	HHV, MJ/kg	Mass, %	HHV, MJ/kg
Accumulator	52.5	22.79	49.0	22.28	40.1	28.43	35.4	28.67
Reactor auger	13.1	24.63	10.4	24.98	10.4	28.62	15.1	28.54
Feed auger	0.4	24.95	0.1	24.74	0.2	28.96	1.6	28.23
Wall residues	3.7	23.12	1.4	24.49	2.9	27.86	2.1	26.93
Total recovery	69.7		60.9		53.6		54.2	

Energy content of starting feedstock was 20.2 MJ/kg

Mass yields are expressed as percent, relative to starting dry feedstock

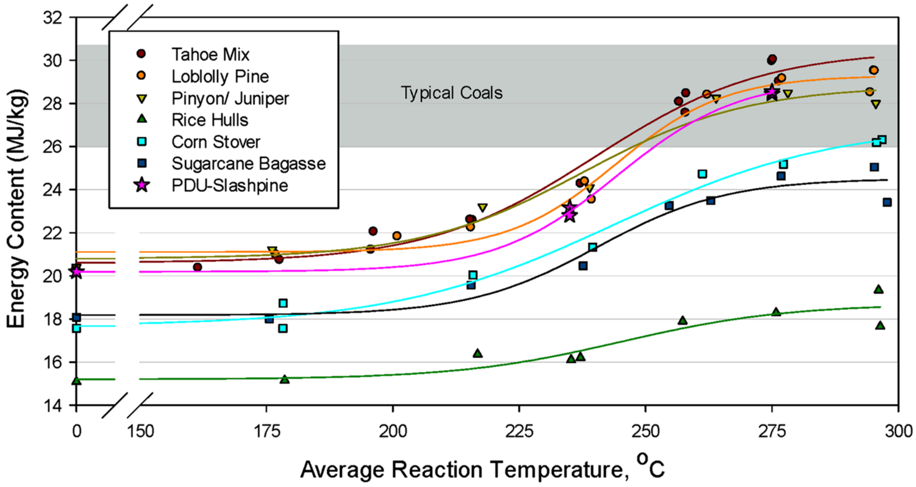


Fig. 3 Effect of HTC reactor temperature on energy content of produced hydrochar. *Star symbols* represent PDU experiments in the present study using Slash Pine feedstock; all other experiments were conducted previously using a stirred, 2-L Parr reactor, with a 30-min hold time

PDU experiments. Ultimate analyses of the four hydrochar products are summarized in Table 3, along with the energy content, mass yield, densification factor, and O/C ratios. (These values are all based upon analyses of the combined four hydrochar fractions obtained from each experiment, as explained above.) The results indicate that for most hydrochar measurements, there was very little difference between the slow and fast auger speeds. (The rather large difference shown for mass yield at 235 °C may result from an erroneous measurement, possibly due to the presence of broken glass marbles collected with the hydrochar.) The energy densification factors of the hydrochars at 235 and 275 °C were approximately 1.1 and 1.4, respectively, which are in good agreement with values determined previously using a 2-L Parr reactor [10, 11]. Also, the O/C ratios of the PDU-generated hydrochars are in good agreement with those observed from the same Parr experiments.

Table 3 Properties of solid hydrochar from PDU treatment of Slash Pine

	Feedstock	235° C reactor temp.		275 °C reactor temp.	
		Slow	Fast	Slow	Fast
HHV, MJ/kg	20.19	23.17	22.80	28.44	28.56
Mass yield, %		69.7	60.8	53.6	54.2
Energy densification		1.15	1.13	1.41	1.41
Elemental analysis, %					
C	49.35	57.08	56.53	69.34	67.05
H	6.21	5.83	5.81	5.10	4.88
N	0.01	0.09	0.10	0.18	0.17
S	–	–	–	–	–
O	45.98	37.37	39.54	25.49	23.63
O/C ratio	0.70	0.49	0.52	0.28	0.26

Sulfur levels were all below detection

Mass yields are expressed as percent, relative to starting dry feedstock

Table 4 NVR and TOC yields in aqueous product fractions from PDU treatment of Slash Pine

Target temp, °C	Auger speed	Collection location	NVR, %	TOC, %	pH
235	Slow	In-situ	0.11	0.09	NM
		Accumulator	1.46	1.08	NM
		Reactor	1.61	2.45	NM
		Total	**3.07**	**3.62**	–
235	Fast	In-situ	NM	0.00	NM
		Accumulator	NM	3.80	NM
		Reactor	NM	2.22	NM
		Total	–	**6.02**	–
275	Slow	In-situ	NM	0.00	NM
		Accumulator	1.89	1.40	3.46
		Reactor	2.72	3.05	3.23
		Total	**4.61**	**4.45**	–
275	Fast	In-situ	0.01	0.01	NM
		Accumulator	3.15	1.98	3.66
		Reactor	5.65	3.71	3.77
		Total	**8.80**	**5.70**	–

Results expressed as mass percent relative to starting dry feedstock

NM not measured

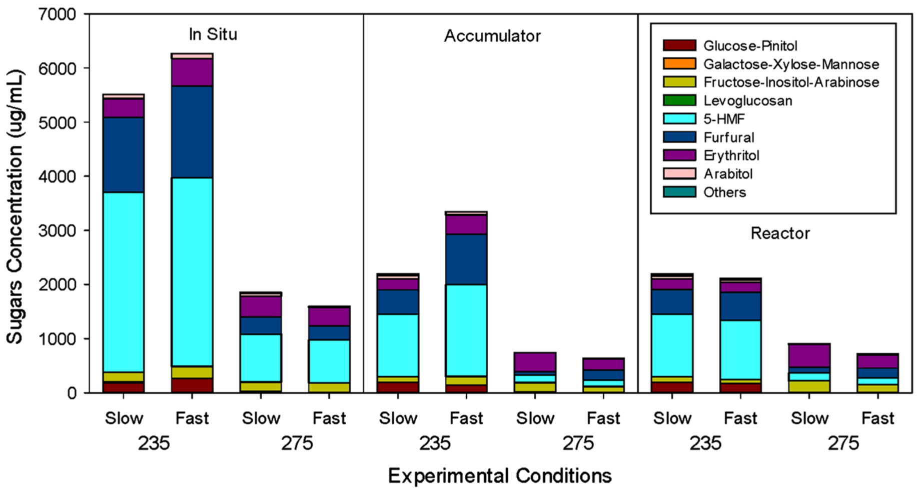
Aqueous Products

Non-volatile residue (NVR) and total organic carbon (TOC) analyses of the aqueous products from the PDU experiments are summarized in Table 4. (Analytical methods for determining NVR and TOC have been reported previously [11].) In each experiment, three aqueous fractions were evaluated: (1) a small "in situ" sample collected in the liquid sampling system pressure vessel while the PDU was still hot and pressurized, (2) the contents of the accumulator (after cooling), and (3) the liquid that was drained from the bottom of the reactor (after cooling). The results in Table 4 are expressed as mass percent of starting dry feedstock. On this basis, the amounts measured for the in situ samples are very small, because the total in situ volume was only about 100-mL, while much larger aqueous sample volumes were collected from the accumulator and the reactor (6–10 L in each case). Therefore, it is expected that most of the NVR and TOC would be found in the accumulator and reactor samples. From each experiment, total NVR and total TOC were in reasonable agreement, which is consistent with results obtained previously using three woody feedstocks in a 2-L stirred Parr reactor [11]. Also, relatively little effect of temperature on NVR and TOC was observed, which was also the case in the previous Parr experiments. However, the total amounts of NVR and TOC from these PDU experiments were somewhat lower than in the previous experiments; with a range of 3–8 % from these PDU experiments compared to 7–11 % from the previous Parr experiments.

Sugars

Sugars were also analyzed in each of the three aqueous product fractions, using the HPLC procedure described previously [11]. These results are shown graphically in Fig. 4. Although the concentrations of sugars were highest in the in situ samples, these samples did not contribute a significant fraction of the total sugars, due to their small volumes. Nevertheless, these higher concentrations suggest that the sugars produced in the HTC process are relatively unstable at the high process temperatures employed. The in situ samples cool quickly after they are collected, thereby quenching the degradation reactions and retaining higher sugar concentrations, whereas the reactor and accumulator samples cool much more slowly, as they

Fig. 4 Sugars in aqueous PDU fractions, measured as concentration in aqueous sample



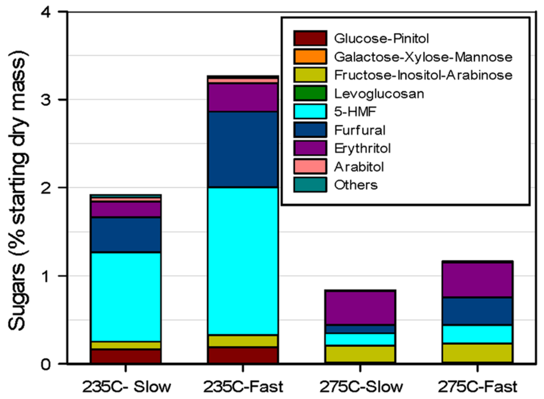


Fig. 5 Total sugars measured in combined aqueous fractions from PDU experiments

remain within the highly insulated body of the PDU. The instability of these sugars can also be seen by comparing the results from HTC experiments at different temperatures. As shown in Fig. 4, considerably higher sugar concentrations were measured in all three aqueous fractions from experiments at 235 °C as compared to 275 °C.

The sugar results also suggest that auger speed had an effect upon the HTC products. Figure 5 shows the total sugars measured from each experiment (sum of the in situ, accumulator, and reactor fractions), expressed as mass percent of starting dry feedstock. At both reactor temperatures, sugar recoveries were higher with the fast auger speed compared to the slow speed. This is attributed to differences in residence time within the hot reaction zone. With a faster auger speed, sugars remaining within the solid hydrochar matrix are removed from the reaction zone more quickly, and quenched within the accumulator.

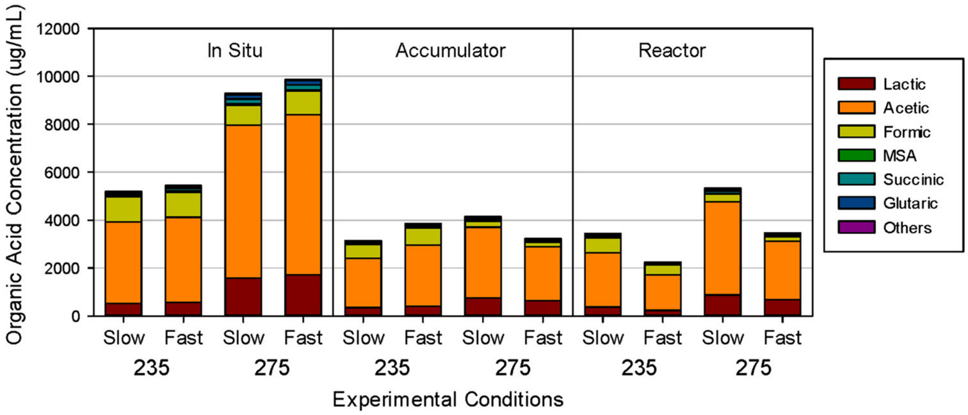
The effects of process temperature upon sugar recoveries are very similar to what was observed previously in 2-L Parr reactor experiments [10, 11]. The effects of temperature upon sugar compositional profiles are also similar between the PDU and the 2-L Parr experiments. As shown in Fig. 5, at 235 °C furfural and 5-HMF are the major species present. At higher process temperature, these compounds are mostly degraded, while erythritol becomes more prominent. This same behavior was observed in previous experiments with the 2-L Parr reactor when using woody biomass feedstocks [11]. One difference between the PDU results here and the earlier 2-L Parr results is that the total amount of sugars recovered was greater from the Parr reactor. For example, with three different woody feedstocks treated at 235 °C in the Parr reactor, total sugar recoveries were 4–8 % of starting dry mass, whereas only 2–3 % was observed from the PDU. One reason for this difference may be the long cool-down period in the PDU, as compared to the Parr reactor, which was quenched by immersing in an ice bath once the desired reaction period had elapsed.

Organic Acids

Organic acids were also measured in each of the three aqueous fractions collected from these PDU experiments. Using an ion chromatography (IC) method described previously [10, 15] the concentrations measured in each fraction are shown in Fig. 6, and the total yields from each experiment are shown in Fig. 7. In all samples, acetic acid was the dominant constituent, although formic acid and lactic acid are quite significant in some cases. This is consistent with previous results obtained from a 2-L Parr reactor [11].

Reaction temperature clearly affected organic acid yields, with higher overall yields being seen at higher temperature. This is expected, since degradation of the sugars (as noted above) leads to increased organic acid concentrations. The effect of auger speed (residence time) is not as clear. Faster auger speed appeared to give slightly higher organic acid yields at both temperatures. This is somewhat surprising, as slower auger speed might be expected to result in greater degradation of the

Fig. 6 Organic acid concentrations in aqueous PDU fractions from HTC treatment of Slash Pine



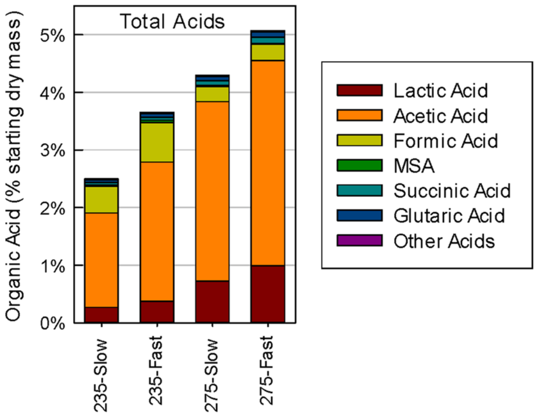


Fig. 7 Organic acid yields in aqueous PDU fractions from HTC treatment of Slash Pine

lignocellulosic material, and hence greater acid yields. Additional experiments, with better control of operating parameters, are necessary to accurately determine the true effects of reaction time upon organic acid yields in the PDU.

Total acid recoveries, and the compositional profiles of these acids, are quite similar to results obtained from earlier Parr reactor experiments. In all cases, acetic acid was the dominant compound seen. (A small amount of levulinic acid was likely present as well, but could not be quantified easily, as it co-elutes with acetic acid under the chromatographic conditions used.) At the lower temperature, a significant amount of formic acid was seen, but this decreased at higher temperature. In contrast, lactic acid increased with reaction temperature. Similar changes in compositional profiles were seen in the earlier Parr experiments with woody feedstocks. The total acid yields in the Parr experiments were 4–6 % at 235 °C and 6–8 % at 275 °C, which are somewhat higher than the yields observed from these PDU experiments.

Gaseous Products

As is well known from the literature [1, 2, 5] and from our previous experience [10, 11], CO_2 is the dominant gaseous species produced by HTC treatment of biomass feedstocks. To confirm this with the PDU, an HTC experiment was conducted using Pinyon-Juniper as feedstock and a reaction temperature of 235 °C. After cooling overnight, gaseous products were collected by sampling out of Port P-1A (Fig. 1) into a series of ten 10-L Tedlar bags. The first four bags were filled completely by the pressurized gas within the PDU. Bags 5–10 were filled by sparging helium into the PDU at Ports P-4E and P-5D. All 10 bags were analyzed for CO and CO_2 using a GC procedure that has been reported previously [11]. Results indicated that Bags 1–4 contained approximately 3 % CO, with the remainder being CO_2. Bags 5–10 (filled with helium sparging) contained incrementally reduced amounts of CO and CO_2. The relative reduction of CO concentration was more rapid than the reduction of CO_2, as expected due to the much higher water solubility of CO_2. The CO concentration dropped to near zero by Bag 7, while the CO_2 concentration was still about 8 % in Bag 10. By combining the gas measurements from all 10 bags, the yields of CO and CO_2 were determined to be 0.10 and 5.56 %, respectively (expressed on a mass basis relative to the starting mass of dry Pinyon-Juniper feedstock). These yields are in good agreement with results obtained from earlier HTC experiments using a 2-L Parr reactor [11].

To further understand the gas composition produced by HTC treatment of Pinyon-Juniper in the PDU, GC-MS analysis was conducted on the Bag 1 sample (collected without helium sparging). As shown in the total ion current (TIC) chromatogram of Fig. 8, these trace gas species are dominated by furan and methyl furan. More detailed results are presented in the Supplementary Material, where over 50 compounds are identified.

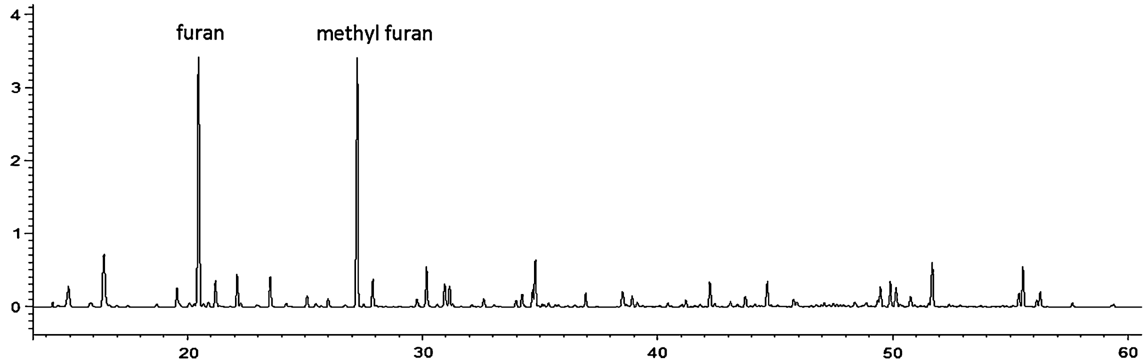


Fig. 8 Gas chromatogram from headspace analysis of PDU (HTC of Pinyon-Juniper at 235 °C). See Supplementary Material for identification of all major constituents

Conclusions

In this work, a laboratory-scale, semi-continuous PDU was designed and built to convert raw lignocellulosic biomass feedstocks into a homogeneous, energy-dense, solid char product by means of HTC. Approximately 3 kg of feedstock can be processed in a single run, which produces sufficient product for subsequent use. The main component of the PDU is a tubular pressure vessel that is rated to operate at pressures up to 1,300 psi. This unit includes two augers: one to drive raw biomass into a reaction zone containing hot, compressed water; the other to remove the solid product from the reactor zone and deposit it into a collection vessel that is maintained at a lower temperature.

The degree of energy densification varies with process temperature. Process time also affects energy densification, but appears to be of secondary importance. To demonstrate satisfactory operation of the PDU, micro-chips (1/4–3/8 in.) of Slash Pine were treated at 235 and 275 °C for relatively short times (5–10 min). Compared to the energy content of the raw feedstock, the hydrochar products had increased energy densities of about 12 and 40 % at 235 and 275 °C, respectively. The hydrochar produced at 275 °C had an energy content of about 28 MJ/kg (HHV), which is similar to low grade coals.

These energy densification results obtained from the PDU are in good agreement with those obtained earlier using small-scale (2-L) Parr pressure reactor experiments that were conducted over a wide range of process temperatures. Gaseous product yields (CO and CO_2) were also similar to those observed in earlier experiments. Trace levels of organic compounds in the gas phase were analyzed by GC–MS and found to be dominated by furans. Characterization of aqueous products from the PDU experiments (TOC, NVR, and sugars) also showed good agreement with earlier Parr reactor experiments. Taken together, these results suggest that the PDU provides a realistic scale-up of the HTC process, and give us confidence that the Parr reactor results obtained with other feedstocks will also translate to the PDU.

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